



Quality assessment of surface waters and sediments of a hydrocarbon contaminated Mangrove wet land

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The study on quality assessment of surface waters and sediments of a hydrocarbon contaminated mangrove wetland that is between longitude (6°45', 6°51')E and latitude (4°35', 4°48')N in the Niger Delta, Nigeria was carried out using standard methods. The data obtained indicated variability in most of the quality characteristics in the sediments and surface waters of the area under investigation. Of all the parameters studied, it is only pH value 7.0 ± 0.13 , sulphate ions - $367.9 \pm 366.2 \text{ mg/l}$, calcium ions - $0.911 \pm 0.630 \text{ meq/100ml}$ and magnesium ions - $3.244 \pm 2.350 \text{ meq/ml}$ that are significantly higher ($P < 0.05$) in the surface water than in the sediments 4.4 ± 0.65 , $20.7 \pm 9.5 \text{ mg/kg}$, $0.262 \pm 0.084138 \text{ meq/100g}$ and $0.736 \pm 0.138 \text{ meq/100g}$ respectively. Apart from salinity, all other parameters were significantly higher in the sediments than in the surface waters, seasonally (dry and wet) there were significant differences ($P < 0.05$) of most of the parameters in both media apart from pH value and potassium ions in the surface water and phosphate and nitrate ions in the sediments. The results of the study have shown that most of the parameters in the sample stations are higher than the control station, related studies and some regulatory limits. The stations with higher values of these parameters are mostly stations with more anthropogenic activities. There is therefore need for continuous monitoring to be carried out to ascertain the long-term impact of anthropogenic inputs to take remedial measures so as to ensure the health of aquatic life.

INTRODUCTION

The occurrence of crude oil in the Niger Delta with its concomitant petroleum industrialization has resulted in the generation of enormous waste products (World Bank, 2005), most of which are not efficiently disposed of (UNEP, 2011). Some of the serious environmental problems that have arisen in the marine environment as a result of the activities of up and down stream petroleum industries include, depletion of marine organisms, destruction of algae and some planktons as well as the interference with spawning areas on the sea bed (Jack *et al.*, 2005, Emoyan *et al.*, 2006). In addition to these waste products from the petroleum industry there are also diverse sorts of wastes that ultimately get into the aquatic ecosystem through surface water runoff, industrial effluents, agricultural and chemicals wastes, sewage outfalls, urban runoff, rivers and atmospheric deposition (Obire and Amusan, 2003, Avwiri, 2005). In coastal ecosystems, sediments play an important role in biogeochemical cycles and also as 'sink' to these wastes (Pekey, 2006, Marchand *et al.*, 2006, Sawant *et al.*, 2011, Janadeleh, *et al.*, 2016). Much of allochthonous material is incorporated in the sediments,

through assimilation, adsorption and direct sedimentation processes of suspended particulates, so they act as a trap of detritus material and mineral nutrients supply, also organic matter is mineralized and dissolved nutrients exchanged within the interface (Orji, *et al.*, 2013).

Contaminants concentration in the water column can be relatively low in some cases, but the concentrations in the sediment may be elevated (Karbassi, and Pazoki 2015). It has been observed that due to temporal and spatial variability in water column, it is always problematic to obtain representative samples to actually show the true concentration of contaminants in surface water, on the other hand sediments integrate contaminants over time and are in constant flux with the overlaying water column; hence the analysis of chemical parameters in sediments permits detection of contaminants that may be either absent or having low concentrations in the water column (Boreretzen and Albu, 2002, Sawant *et al.*, 2011, Orji, *et al.*, 2013).

The mangrove wetland of the Niger Delta occupies intertidal land in a broad zone of tidal creek behind the barrier islands. This is different from what obtains in some other regions, where mangrove forests occur only as a thin band along the coast and are exposed directly to seawater. The mangrove floor is important to innumerable smaller flora and fauna, and so ultimately the food chain leading to man. Many invertebrate species such as crabs and certain shrimps live hidden in burrows. The firm ground of the mangrove floor consists of peat formed by

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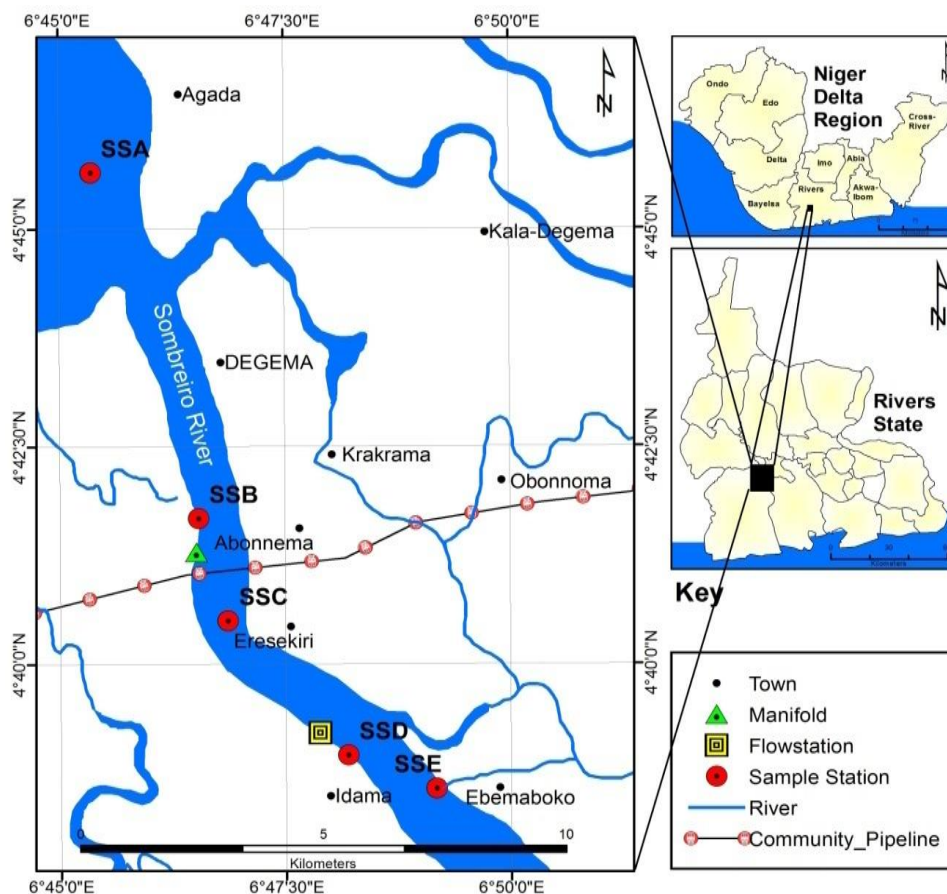


Figure 1 Map of the study area

accumulated rootlets of *Rhizophora*. Whereas the effects of oil on the mangrove environment is well known and some studies have been carried out in the Niger Delta (Ezekiel *et al.*, 2002, Osuji and Onojake 2004, Jack *et al.*, 2005, Osuji and Ezebuiri 2006), available information is still not sufficient to assess the present condition of the region with respect to oil spills. Therefore the periodic monitoring and analyses of typical and potential pollutants are essential for effective management of any impacted environment. In a similar study carried out on total hydrocarbon levels (THC) in this same study area it was observed that the THC levels of the surface water exceeded the national regulatory limit of 10.0mg/l (FMENV 1991) while the mean value of THC in the surface sediments is 2045.1 ± 1611.5 (Howard *et al.*, 2012). Other studies within the Niger Delta also indicate high levels of THC (Osuji and Onojake 2004, Jack, *et al.*, 2005, Osuji and Ezebuiri 2006, Ibigoni *et al.*, 2009). It is for these reasons that some quality parameters of the surface waters and sediments of the upper reaches of Sombreiro river mangrove wetland that houses the Idama oil flow station and other adjoining crude oil installations were determined to ascertain the quality of the area.

RESULTS AND DISCUSSION

The mean concentrations of the physical and chemical characteristics in the surface waters and sediments of the study area and a summary of the statistical analysis of the data are as shown in Table 1. Figures 2 and 3, shows the seasonal mean variations of the physical and chemical characteristics of the surface waters and sediments of the study area respectively.

The pH values for the study area were stable across the stations and within sampling periods for both media. This means there was no

significant difference between the stations and within both media; however there was significant difference between the media. The mean pH values for the study period across the stations was 7.00 ± 0.13 for the surface water and 4.4 ± 0.65 for the sediments. This implies that the water is neutral whereas the sediment is acidic.

Generally, fluctuations in pH values during different seasons of the year is attributed to factors like removal of CO_2 by photosynthesis through bicarbonate degradation, dilution of seawater by freshwater influx, reduction of salinity and temperature and decomposition of organic matter (Rajasegar, 2003). Again the low value of pH indicating acidic condition in the sediments may be due to the oxidation of FeSO_4 and FeS to H_2SO_4 (Masoud *et al.*, 2005). In addition, soil acidity may have resulted also from decomposition of mangrove litter. pH is an important attribute of sediments/soils because it affects the solubilities of the various ionic species, the bonding of the ions to exchange sites and microbial activity in the soil (Babatunde and Ajibola 2009; Karbassi and Heidari 2015).

In moderately neutral to strongly acidic soils for instance, phosphates becomes less available through interactions with $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. At high pH, phosphates become increasingly insoluble because of their interactions with Ca^{2+} to form apatite and other precipitates (Babatunde and Ajibola 2009). The pH values of the surface waters of this study are typical of tropical aquatic environment; however those of the sediments are lower than those of Davies & Abowei (2009) and Saravanakumar (2008) where there were no hydrocarbon contaminations but are at par with those of Osuji & Ezebuiri (2006) where there was contamination.

The mean electrical conductivity values of the stations varied from $8.2 \pm 8.61 \text{ mS/cm}$ (Station A) to $12.4 \pm 10.67 \text{ mS/cm}$ (Station E) for the

Table 1 The physical and chemical characteristics of the surface water and sediments of the study area

Quality Parameters	Media	Stations					Mean±std
		A	B	C	D	E	
pH	S. Water	7.0±0.15	7.0±0.13	7.0±0.16	7.0±0.08	7.1±0.15	7.0±0.13^A
	Sediment	4.2±0.79	4.5±0.70	4.4±0.61	4.4±0.62	4.7±0.80	4.4±0.65^B
Salinity (‰)	S. Water	4.7±5.16	6.4±6.02	6.5±5.84	7.0±6.57	7.3±6.62	6.38±5.47^A
	Sediment	4.7±4.16	5.5±2.85	5.2±1.41	6.2±2.04	7.3±1.95	5.8±2.54^A
EC (mS/cm)	S. Water	8.2 ±8.61	9.9 ±10.87	11.2 ±9.49	11.9 ±10.60	12.4 ±10.67	10.7±9.10^B
	Sediment	13.3±12.1	15.1±8.63	11.7±3.14	13.9±4.11	19.1±6.83	14.6±7.27^A
PO₄³⁻ (mg/l)	S. Water	0.029±0.02	0.021±0.01	0.026±0.02	0.019±0.01	0.029±0.01	0.023±0.01^B
	Sediment	0.558±0.17	0.517±0.09	0.576±0.06	0.453±0.05	0.533±0.08	0.527±0.10^A
SO₄²⁻ (mg/l)	S. Water	251.3±275.6	362.8±381.2	404.5±421.1	339.2±356.4	481.8±533.9	367.9±366.2^A
	Sediment	16.8±9.0	17.2±9.2	21.8±6.6	23.8±10.5	23.9±13.5	20.7±9.5^B
Cl⁻ (mg/l)	S. Water	2198.6±1607	3305.5±2271	3244.4±2273	3114.6±2407	4237.0±2886	3220.0±2170^B
	Sediment	11026.4±9784	12118.5±6543	12972.5±3741	14868.9±5607	17665.8±6396	13730.4±6422^A
NO₃⁻ (mg/l)	S. Water	0.210±0.170	0.202±0.213	0.232±0.199	0.193±0.171	0.290±0.115	0.226±0.161^B
	Sediment	11.644±5.041	10.564±7.00	11.723±4.369	9.630±6.052	12.693±6.324	11.251±5.294^A
Mg²⁺ (meq/100ml)	S. Water	3.097±5.164	2.998±4.330	2.941±3.510	3.678±5.179	3.508±4.894	3.244±4.150^A
	Sediment	0.736±0.567	0.734±0.448	0.624±0.396	0.887±0.501	0.699±0.381	0.736±0.421^B
K⁺ (meq/100ml)	S. Water	0.001±0.00	0.001±0.00	0.001±0.00	0.001±0.00	0.001±0.00	0.001±0.00^B
	Sediment	0.040±0.012	0.047±0.009	0.044±0.031	0.042±0.014	0.037±0.018	0.042±0.017^A
Ca⁺ (meq/100ml)	S. Water	0.765±0.841	0.964±1.290	1.170±1.780	0.926±1.306	0.730±0.816	0.911±1.129^A
	Sediment	0.199±0.122	0.266±0.107	0.279±0.121	0.327±0.121	0.238±0.063	0.262±0.106^B
Na⁺ (meq/100ml)	S. Water	0.022±0.014	0.026±0.014	0.027±0.019	0.024±0.013	0.022±0.008	0.024±0.013^B
	Sediment	0.714±0.913	0.799±0.937	0.940±1.014	0.013±0.987	0.931±0.860	0.870±0.845^A
TOC (%)	S. Water	1.01±0.5	1.60±0.86	0.78±0.78	1.85±0.26	1.29±0.62	1.31±0.70^B
	Sediment	1.92±0.79	2.44±1.25	1.08±0.92	2.64±1.31	1.48±0.62	1.91±1.08^A

Values with different characters (mean ±std) are significantly different (P<0.05)

surface water and that of the sediments is 13.3±12.1mS/cm (Station A) to 19.1±6.83mS/cm (Station E) with the Station E's value showing great significant difference at p<0.05 for both media. The conductivity values for stations B, C, and D showed no significant difference in both media as shown in Table 1. The mean conductivity value across the stations was 10.7±9.10mS/cm for the surface water and 14.6±7.27mS/cm for the sediments. The dry season's mean values were significantly different from the wet season for both media as shown in Figures 1 and 2. The high electrical conductivity values for the surface water indicates that the study area is brackish as values above 1.0mS/cm electrical conductivity are regarded as brackish (SAWQG 1996). Again from the trend Sample Station E which have a higher conductivity value is more brackish than that of station A, implying that station E is closer to the ocean than station A of the study area. The values of this study (surface water) compares favorably with the conductivity values recorded by Abowei and George (2010) in Okpoka Creek, Niger Delta, Ekeh and Sikoki (2003) in the New Calabar River, (Zabbey, 2002) in Woji Creek, but those of the sediments are higher than those of Davies and Abowei (2009).

The mean Salinity of the study area ranged from 4.7±5.16 ‰ (Station A) to 7.3±6.62 ‰ (Station E) for surface water and 4.7±4.16 (Station A) to 7.3±1.95‰ (Station E) for the sediments. Again station E's value for both media are significantly different from that of station A, whereas the salinity values of B, C, and D showed no significant difference in both media as shown in Table 1. There was no significant mean difference between both media (Table 1), however the high salinity values across the stations for both media indicates that the study area is brackish in nature as evidenced by the high electrical

conductivity values. This agrees with the fact that waters with salinity below 1‰ are fresh and waters with salinity higher than 1‰ are brackish/marine (SAWQG 1996). These mean salinity values compares favorably with those reported by Hart and Zabbey (2005), Emmanuel and Onyema (2007), Abowei and George (2009), Deekae *et al.*, (2010) and Nkwoji *et al.*, (2010).

Phosphate (PO₄³⁻) in surface water ranged from 0.019 ± 0.01 (Station D) – 0.029±0.1mg/l (Station E and A) with an average of 0.035±0.001mg/l for the wet season and 0.012±0.005mg/l for the dry season whereas in the sediment the range is 0.453±0.05 (Station D) – 0.576±0.06mg/kg (Station A) with an average of 0.5±0.1mg/kg for the wet season and 0.5±0.08mg/kg for the dry season. From the result the sediments of the study area has more phosphate than the surface water, however there are no significant differences between the stations for both media but for the surface water we have a significant difference between the wet and dry seasons. The high level of phosphates in the wet season corroborates the findings of similar study (Howard *et al.*, 2006) in the Niger Delta. This could be due to high influx of surface runoffs into the river during the rainy season than in the dry season. Again the relative high content of phosphate in the sediments of the study area explains the role it plays as a nutrient for the growth of mangrove plants in an aquatic environment (Saravanakumar *et al.*, 2008). The value of this present findings are lower than that obtained by Olajire and Imeokparia (2001) who reported that PO₄ levels fluctuate between 0.46 and 0.59 mg/L in the upstream and downstream of the Osun river, Nigeria and that of Saravanakumar *et al.*, (2008) but are at par with an earlier study (Howard, *et al.*, 2006). The levels of phosphate

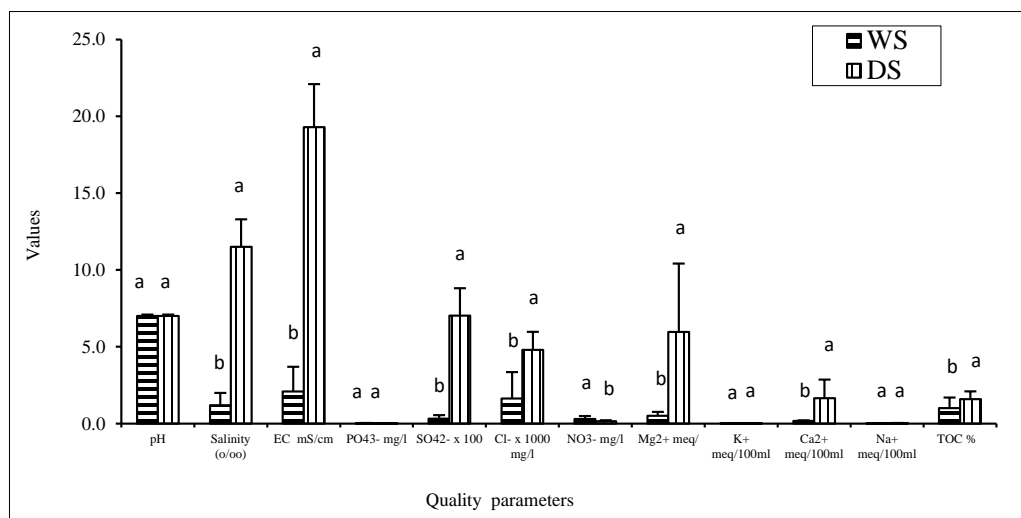


Figure 2 Seasonal mean variation of the physical and chemical characteristics of the surface waters of the study area (Bars with different characters (alphabets) are significantly different ($P < 0.05$))

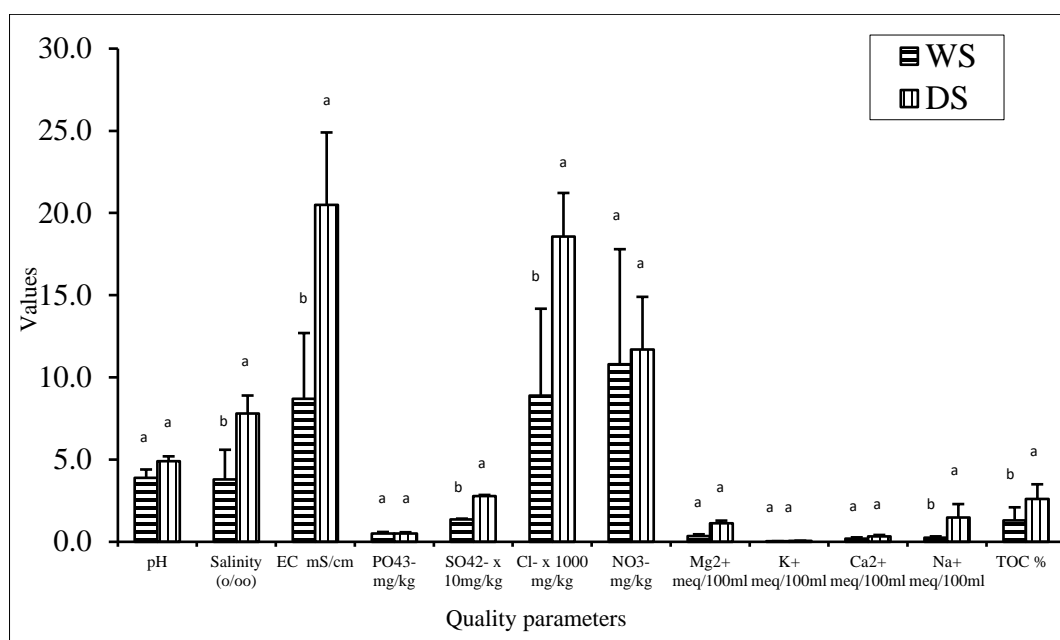


Figure 3 Seasonal mean variation of the physical and chemical characteristics of the sediments of the study area (Bars with different characters (alphabets) are significantly different ($P < 0.05$))

in the entire water sampling stations were below the WHO maximum permissible limit of 5 mg/L phosphate SAWQG (1996).

Sulphate (SO_4^{2-}) ranged from 251.0 ± 275.6 (Station A) – 481.8 ± 537.9 mg/l (Station E) in the surface water with an average of 31.9 ± 23.5 mg/l for the wet season and 704.0 ± 177.4 mg/l in the dry season whereas in the sediment the range is 17.2 ± 9.2 (Station A) – 23.9 ± 13.5 mg/kg (Station E) with an average of 13.6 ± 5.1 mg/kg for the wet season and 27.8 ± 7.2 mg/kg for the dry season. The sulphate levels among the stations showed high variability, which could be due to the surface runoffs from the inland areas into the river unlike in the case of phosphate, we have high level of sulphate in the surface water than in the sediments, again we have high sulphate levels in the dry season than in the wet season which was also similar to earlier findings (Howard *et al.*, 2006). The values obtained in the surface water of this study is higher than that reported by Fytianos *et al.* (2001), Helen *et al.*, (2005),

Babtunde and Ajibola (2009) but lower than that reported by Howard *et al.*, (2006). Sulphate is the most important form of inorganic sulphur in soils and is the most readily available form to plants because sulphates are resistant to leaching. The fate of sulphate in the soil is influenced by many chemical, biological and physical factors and the ability of the soil to absorb the sulphates occurs above a pH of 6.5 but adsorption increases as pH decreases (Cichota *et al.*, 2004). The levels of sulphate in the surface water samples in the entire sampling stations were above the 200 mg/l WHO maximum permissible levels (SAWQG 1996).

Nitrate levels in the five sampling stations fluctuates between 0.193 ± 0.171 (Station D) – 0.290 ± 0.115 mg/l (Station E) with an average of 0.296 ± 0.199 mg/l in the surface water for the wet season and 0.155 ± 0.066 mg/l dry season, whereas in the sediment the range is 9.63 ± 6.05 (Station D) – 12.693 ± 6.32 mg/kg (Station E) with an average of 10.8 ± 7.0 mg/kg for the wet season and 11.7 ± 3.2 mg/kg for the dry

season. Nitrate is an essential nutrient for many photosynthetic autotrophs and in some instances, functions as a growth-limiting nutrient. It is used by algae and other aquatic plants to form plant protein which, in turn, can be used by animals to form animal protein. Nitrate is a major ingredient of farm fertilizer and is necessary for plant uptake and is essential to plant growth (Helen, *et al.*, 2005). When it rains, varying nitrate amounts wash from farmland in to water body. Nitrates stimulate the growth of plankton that provides food for fish. This may increase the fish population. However, if algae grow too wildly, oxygen levels will be reduced and fish will die. From the results the sediment load of nitrate in the study area is higher than that of the surface water. The possible reason could be due to decomposition of planktonic detritus that may be present in the environment, variation in phytoplankton excretion, oxidation of ammonia and reduction of nitrate (Rajasegar, 2003). For each of the media there were no significant differences between the stations, but station E had the highest values for both media seasonally. The higher level of nitrate in the surface water during the wet season which is in line with the findings of Savanakuma *et al.*, (2009), Gowada, (2001), Howard *et al.*, (2006) could be due to rainfall and land runoff (Savanakuma *et al.*, 2009).

Chloride ion varies from $2,198.0 \pm 1607.0$ (Station A) – $4,237.0 \pm 2886.0$ mg/l (Station E) in the surface water with an average of $1,631.5 \pm 1,724.3$ mg/l for the wet season and $4,808.5 \pm 1168.0$ mg/l for the dry season whereas in the sediment the range is $11,026.4 \pm 9,784.0$ (Station A) – $17,665.8 \pm 6396.0$ mg/kg (Station E) with an average of $8,888 \pm 5290$ mg/kg for the wet season and $18,571.9 \pm 2,648.5$ mg/kg for the dry season. The chloride levels are highest in station E for both media indicating that the value increases downstream and these high values corroborates those of the conductivity and salinity values that were also high also indicating the brackish status of the area (SAWQG 1996). Cl^- is easily leached at neutral and alkaline pH values and hence it is not adsorbed on soil particles. At high concentrations, chlorides interact with metals to enhance corrosion by accelerating oxidation (SAWQG 1996). The levels of the chlorides in the surface waters of this study are higher than those of Howard, *et al.*, (2006) and those of the sediments are also higher than that reported by Babatunde & Ajibola (2009). As reported by Babatunde & Ajibola (2009) chloride concentrations are higher than concentrations of nitrates and sulphates in surface soils which is in conformity with this study in both media.

Available potassium (K^+) in all the stations range from 0.0005 ± 0.0003 (Station C) to 0.0008 ± 0.0004 meq/100ml (Station D) in the surface water; with an average of 0.0005 ± 0.0001 meq/100ml for the wet season and 0.0008 ± 0.0004 meq/100ml for the dry season and 0.037 ± 0.018 (Station E) – 0.047 ± 0.009 meq/100g (Station B) in the sediments with an average of 0.031 ± 0.009 meq/100g for the wet season and 0.052 ± 0.016 meq/100g for the dry season. Stations D and E are significantly higher than the other stations in the surface water but there was none in the sediment. The highest recorded value for sediment is station B. High concentrations of K in stations D, E and B may be due to presence of minerals of weather and release of K ion. These ions are adsorbed onto the cation exchange sites.

Calcium (Ca^{2+}) ion varies from 0.730 ± 0.816 meq/100ml (Station E) – 1.170 ± 1.780 meq/100ml (Station C) in surface water with an average of 0.174 ± 0.040 meq/100ml for the wet season and 1.648 ± 1.219 meq/100ml for the dry season and 0.199 ± 0.122 (Station A) – 0.372 ± 0.121 meq/100g (Station D) in sediments with an average of 0.196 ± 0.077 meq/100g for the wet season and 0.328 ± 0.090 meq/100g for the dry season. From the result shown in Table 1, there was a significant

difference of Ca^{2+} between the dry season and the wet season in both media but the mean values of Ca^{2+} in the surface water is higher than in the sediment. This could be that Ca^{2+} dissolves in the water column more than in the sediments. Again the high values of exchangeable Ca^{2+} in both media is more than other cations apart from magnesium ions which may be due to the amount of exchangeable and solution forms of Ca^{2+} in both media. It can also be attributed to weathering of minerals and their deposition in sediments.

Magnesium (Mg^{2+}) ion fluctuates between 2.941 ± 3.510 meq/100ml (Station C) and 3.678 ± 5.179 meq/100ml (Station D) in the surface waters with an average of 0.521 ± 0.245 meq/100ml for the wet season and 5.968 ± 4.452 meq/100ml in the dry season and 0.624 ± 0.396 (Station C) – 0.887 ± 0.501 meq/100g (Station D) in sediments with an average of 0.348 ± 0.110 meq/100g in the wet season and 1.125 ± 0.166 meq/100g in the dry season. Like in the case of Ca^{2+} , Mg^{2+} ions are significantly higher in the surface water than in the sediments in all the stations. The possible reason for this is that both cations are all exchangeable mostly in solutions. The values obtained in this study are higher than that obtained by Sawant *et al.*, (2011) in the sediments of Tapti River, Maharashtra, India.

Unlike the case of calcium and magnesium ions, sodium ions (Na^+) varies significantly from the sediment to the surface water in all the stations as shown in Table 1. The values range from 0.022 ± 0.008 (Station E) – 0.027 ± 0.019 meq/100ml (Station C) in the surface waters with an average of 0.013 ± 0.003 meq/100ml for the wet season and 0.035 ± 0.009 meq/100ml in the dry season and 0.013 ± 0.987 (Station D) – 0.940 ± 1.014 meq/100g (Station C) in the sediments with an average of 0.013 ± 0.003 meq/100g for the wet season and 0.035 ± 0.009 meq/100g in the dry season. The reason could be due to a mixing effect of fresh water that comes into the study area from the hinterlands and the saline water that comes through the Atlantic Ocean due to tidal movements.

Total organic carbon varied from 0.78 ± 0.78 (Station C) – $1.85 \pm 0.26\%$ (Station D) in the surface water with an average of $1.0 \pm 0.7\%$ in the wet season and $1.6 \pm 0.5\%$ in the dry season and 1.08 ± 0.92 (Station C) – $2.44 \pm 1.25\%$ (Station B) in the sediments with an average of $1.3 \pm 0.8\%$ in the wet season and $2.6 \pm 0.9\%$ in the dry season. As reported by Saravanakumar *et al.*, (2008) and Sawant, *et al.*, (2011) the distribution of TOC closely followed distribution of sediment type i.e. sediment low in clay content was low in TOC value and as the clay content increased, the TOC also increased. Stations C and A that are low in TOC exhibited this feature and this was observed during the field trips of the study. For both media we have the highest TOC values in stations B and D. This may be due to the presence of mangrove and terrestrial detritus in the suspended matter and also due to the fine nature of sediments, high rate of sedimentation, decomposition of mangrove foliage and other vegetative remains in the sediments. For both media the TOC values are lower in the wet season than in the dry season, this is in line with the findings of Saravankumar *et al.*, (2008) in the mangrove zones of Kachchh-Gujarat.

CONCLUSION

The present study indicated variability in most of the physical and chemical characteristics in the sediments and surface waters of the area under investigation. Of all the parameters studied, it is only pH value, sulphate ions, calcium and magnesium ions that are significantly higher ($P < 0.05$) in the surface water than in the sediments. Apart from salinity, all other parameters were significantly higher in the sediments than in the surface waters. Seasonally (dry and wet) there were significant

differences ($P < 0.05$) of most of the parameters in both media apart from pH value and potassium ion in the surface water and phosphate and nitrate ions in the sediments. The results of the study have shown that some of the parameters are higher in the sample stations B, C, D, and E than the control station (A), related studies and some regulatory limits. The stations with higher values of these parameters are mostly Stations B and D with more anthropogenic inputs. There is therefore need for continuous monitoring to be carried out to ascertain the long-term impact of anthropogenic inputs to take remedial measures so as to ensure the health of aquatic life.

MATERIALS AND METHODS

The study area is a mangrove wetland that is intertidal and lies between longitude ($6^{\circ}45'$, $6^{\circ}51'$) E and latitude ($4^{\circ}35'$, $4^{\circ}48'$) N. The Sombriero river system has experienced increase in industrial, municipal and transportation activities and it is one of the most important river systems in the Niger Delta providing nursery and breeding grounds for a large variety of fish species. It is a distributary of the River Niger which arises from northern boundary of Rivers State with Imo State. It is one of the series of the Niger Delta Rivers which drain into the Atlantic Ocean and is connected to other rivers via creeks in the coastal area of the Niger Delta (Ezekiel *et al.*, 2002).

Passengers, goods and services are transported from one place to the other using petrol and diesel powered engine boats and barges. These activities take place on a daily basis. Several flow-stations, manifolds and wellheads dot the river system and pipelines transporting petroleum products. Environmental influences from the Soku Gas Gathering Plant for the Nigerian Liquefied Natural Gas (NLNG) also impact this river system. The river serves as sink for different forms of wastes produced within the catchment area, thus making it vulnerable to contamination. Five sampling stations (SSA, SSB, SSC, SSD and SSE) hereafter referred to as A, B, C, D and E were chosen within the study area as indicated in Figure 1.

Sample Station A (Longitude $6^{\circ}45'$ $21.8''$ E and Latitude $4^{\circ}45'$ $38.8''$ N) is the control station the major activity here is marine transport with outboard petrol engines and also the fermentation of cassava for the production of "fufu"-a familiar food in Southern Nigeria (Ibigoni *et al.*, 2009). Station B ($6^{\circ}46'$ $21.1''$ E and $4^{\circ}41'$ $32.7''$ N) has a pipeline and manifold that transports condensate to Soku gas gathering plant. This station receives the bulk of discharge of waste water runoff from domestic and municipal activities in Abonnema community. Domestic and industrial wastes from Soku and the Gas Gathering Plant also impact much of this station, in addition to the heavy marine transportation activities.

Station C ($6^{\circ}46'$ $51.5''$ E and $4^{\circ}40'$ $29.6''$ N) was at a Fishing Settlement. It is a fast growing settlement where several activities, such as crude oil, diesel and petrol bunkering take place. Station D ($6^{\circ}48'$ $14.0''$ E and $4^{\circ}38'$ $23.5''$ N) was at the Idama Oil Field, operated by one of the major oil companies in Nigeria. There is a flow station (wherein petroleum fluid is partially treated), wellheads and a manifold. There are dredge-spoils and waste pits with flare points, where hydrocarbons and associated emissions are discharged and waste fuels are burnt. Station E ($6^{\circ}49'$ $10.0''$ E and $4^{\circ}38'$ $33.9''$ N) was also a fishing settlement where bunkering activities also takes place. Barges and tug-boats ply through an adjoining creek to the New Calabar River.

Sample collection

Surface water and sediment samples were collected as reported in an earlier study (Howard *et al.*, 2012). Each sample was concurrently collected in triplicates from each station once in three months between July 2006 and June, 2007. Sediment samples were wrapped with polythene bags. All samples were kept on ice and subsequently, transported to the laboratory. In the laboratory (Institute of Pollution Studies Rivers State University of Science and Technology Port Harcourt) the sediment samples were air dried

and sieved with a 200 μ m sieve before analysis, while the water samples were stored in a refrigerator pending when analysis was carried out.

Measurement of chemical parameters of water samples

The pH, electrical conductivity and salinity of the surface waters of the five sample stations were all measured in-situ with a pre-calibrated Wagtech pH/temperature, Conductivity/TDS meter and salinity meters (Wagtech, 2005) for the rainy and dry seasons. In each case the probes were rinsed and left standing in distilled water before being used for further measurements. The chloride content of the water samples was determined by the Argentometric method (APHA, 2005), phosphate was measured by the Stannous chloride method (APHA 2005), Sulphate by the turbidimetric method (APHA 2005) and nitrate by the Brucine method (APHA 2005). Each of the cations was analysed using atomic absorption spectrophotometric method (APHA 2005). Total organic carbon (TOC) was determined by the chromic acid titrimetric method of Walkey and Black manual titration method (Brain 2002).

Measurement of chemical parameters of the sediment samples

50g of sediment was diluted with 100mL of distilled water in a 250mL beaker to produce a ratio of 1:2 mixture (Sawant *et al.*, 2011). This was stirred with a stirring glass rod to homogenize the mixture and then left for 30 minutes to settle. After which, the probes of pre-calibrated pH, salinity and conductivity meters (Palintest/Wagtech Models) were inserted into the mixture and their respective readings recorded. The anions - nitrates, sulphates, phosphates, chlorides and silica in the sediment were analyzed using APHA 4500- NO_3^- B, APHA 4500- SO_4^{2-} B and APHA 4500 - P C, APHA 4500- Cl^- B and APHA 4500- SiO_2 C of APHA (2005). 10mL of sediment solution was transferred into sample curvette. To this was added the contents of reagent Palintest tablets; whether for the nitrates, sulphates, phosphates and chlorides and silica to complex the colors, if any of the nutrients were present in the sample. The readings were taken on the Palintest/Wagtech 7100 photometer. Each of the cations was analysed using atomic absorption spectrophotometric method (APHA 2005).

Total organic matter (TOM) was determined by first determining the total organic carbon and multiplying it by a factor (1.729) using the Walkley-Black manual titration method (Brian, 2002). This method is based on the theory that the colour of a soil sample determines the organic carbon content of that soil. 1g of sediment samples was sieved through a 1.0mm mesh-size sieve and weighed into 250mL conical flask. 10ml of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) and 20mL H_2SO_4 were added and left to stand for 30 min on asbestos after intermittent swirls. 100ml of distilled water (spectator ion) was added. To this was added 3-4 drops of ferrous indicator and titrated with 0.5N $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. If the sediment sample is rich in organic carbon it will assume a greenish cast on adding all reagents and indicators but if it is not rich in organic carbon it will assume an orange colour. Upon titration, an organic carbon rich sediment goes from green to light green and finally to maroon red or brown; that is the end point. A blank titration (without 1g of sediment) was thereafter carried out and percent TOC was calculated as:

$$\% \text{TOC} = \frac{\text{Blank Titre} - \text{Sample Titre} \times 0.003 \times 100}{\text{Sample weight}}$$

All statistical analysis was carried out with the aid of Data Analysis Toolpak in Microsoft office Excell 2003[®] and SPSS. Differences in the levels of the cations within and between the media were separated by Duncan Multiple Range Test (DMRT) at 95% level of probability.

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Article Key words

Anthropogenic, assessment, contamination, hydrocarbon, mangrove wetland

Acknowledgement

The authors wish to appreciate the Staff and Management of Institute of Pollution Studies Laboratory, Rivers State University of Science and Technology, Port Harcourt Rivers State and Water Well Services

Laboratory Effurun Delta State, Nigeria where the analysis were carried out.

Article History

Received: 02 April 2018

Accepted: 31 May 2018

Published: 1 July 2018

Citation

Ehi-Douglas Omone Monica, Briggs Amonia Olulu, Howard Ibigoni Clinton, Abiodun Iyabode Khadijat. Quality assessment of surface waters and sediments of a hydrocarbon contaminated Mangrove wet land. *Discovery*, 2018, 54(271), 254-261

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